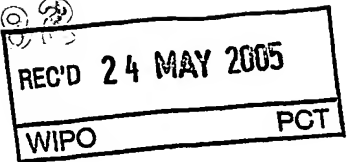


PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PC03023-SY	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 2003/002758	International filing date (day/month/year) 17 December 2003 (17.12.2003)	Priority Date (day/month/year) 30 December 2002 (30.12.2002)
International Patent Classification (IPC) or national classification and IPC IPC⁷: C08L 67/02; C08K 5/29		
Applicant SAMYANG CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 12 sheets.

3. This report contains indications relating to the following items:
 - I. ☒ Basis of the opinion
 - II. ☐ Priority
 - III. ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV. ☐ Lack of unity of invention
 - V. ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI. ☐ Certain documents cited
 - VII. ☐ Certain defects in the international application
 - VIII. ☐ Certain observations on the international application

Date of submission of the demand 23.07.2004	Date of completion of this report 6 April 2005 (06.04.2005)
Name and mailing address of the IPEA/AT Austrian Patent Office Dresdner Straße 87 A-1200 Vienna Facsimile No. 1/53424/200	Authorized officer BAUMSCHABL F. Telephone No. 1/53424/459

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR 2003/002758

I. Basis of the report

1. With regard to the elements of the international application:*

- ☐ the international application as originally filed
- ☒ the description:
pages 2,8-11,13,15, as originally filed
pages 1,3,4-7,12,14,16,18, filed with the demand
pages _____, filed with the letter of _____.
- ☒ the claims:
pages 20, as originally filed
pages _____, as amended (together with any statement) under Article 19
pages 19,21, filed with the demand
pages _____, filed with the letter of _____.
- ☐ the drawings:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____.
- ☐ the sequence listing part of the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____.

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____.
- ☐ the claims, Nos. _____.
- ☐ the drawings, sheets/fig _____.

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 2003/002758

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement			
1. Statement			
Novelty (N)	Claims	1 - 15	YES
	Claims	----	NO
Inventive step (IS)	Claims	7-15	YES
	Claims	1 - 6	NO
Industrial applicability (IA)	Claims	1 - 15	YES
	Claims	-----	NO
Citations and explanations (Rule 70.7)			
<p>JP 4285631 A (abstract), the closest prior art to the present application, discloses bisphenol-A-ethylene oxide which is equivalent (written opinion page 2, D2) to bisphenol-alt-ethylene glycol oligomer of the present application.</p> <p>In JP 4285631 A (abstract) and in the claim 1 of the present application there are given wide ranges (e.g. 5 – 50 mol% of polyoxyalkylenglycol versus 20 – 50 weight% of polyalkylene oxide; 1 – 50 mol% of bisphenol-A-ethylene oxide adduct versus 0,3 – 9,0 weight% of bisphenol-alt-ethylene glycol oligomer) for the components used for producing a thermoplastic polyester elastomer. JP 4285631 A (abstract) teaches the same components (aromatic dicarboxylic acid, diol with low MG, polyalkylene oxide and bisphenol-A-ethylene oxid adduct) for producing a thermoplastic polyester elastomer. With the exception (percentage given in the example is outside the range of 30 – 45 weight%) of the aromatic dicarboxylic acid the ranges for the components given in JP 4285631 A (abstract) and claim 1 of the present application are overlapping and a skilled person could come to the subject matter of the present application according to claims 1 and 4 to 6 without an inventive step. Variation of given components is not seen to be inventive.</p> <p>Some of the thermoplastic elastomer resins of claim 1 have an inherent viscosity (I.V.) of 1.6 – 1.8 dl/g. This is a physical property depending on the chemical composition of the resins. Using the same range of contents for the components which is within the knowledge of a skilled person result in resins with the same specific properties. The use of small quantities of glycerol is not mentioned in JP 4285631 A (abstract) but it is not considered to be inventive alone to use glycerol in "polydiolic mixtures".</p> <p>US 3 723 568 A and JP 60090249 A (abstract) are not based on bisphenol-alt-ethylene glycol oligomer.</p> <p>Based on this argumentation the subject matter of claims 1 to 6 of the present application is considered to be new but not involving an inventive step.</p>			

INTERNATIONAL PRELIMINARY EXAMINATION REPORTInternational application No.
PCT/KR 03/02758**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Box V (page 1)

The subject matter of the present application according to claims 7 to 12 refer to modifications of the resin according to claim 1 and specific properties of such resins as melt index ratio or inherent viscosity. None of the documents cited in the search report covers all elements. Therefore claims 7 to 12 are considered to be new.

US 4 071 503 A discloses a process for preparing polycarbodiimide modified thermoplastic polyesters having increased intrinsic viscosity. US 4 071 503 A discloses that carbodiimide may be prepared by using diisocyanate, but does not disclose that diisocyanate could be directly reacted.

EP 0 357 194 A1 relates to thermoplastic copolyester-carbodiimide blends but does not teach the use 0.1 – 5.0 weight % of diisocyanate as component.

US 5 733 986 A relates to specific polyester elastomers with higher melt viscosity. US 5 733 986 A does not cover the use of carbodiimide.

EP 0 357 193 A relates to thermoplastic copolyester-carbodiimide blends but does not teach the use 0.1 – 5.0 weight % of diisocyanate as component.

Due to the great amount of possibilities of combining components given in the documents and the specific problems (residence time in the extruder, poor productivity and so on) mentioned in the written opinion it is not likely to come to the subject matter of the present application according to claims 7 to 15 by combining the state of the art of documents given in the search report.

Therefore the subject matter of the present application according to claims 7 to 15 involves an inventive step.

Industrial applicability is given.

23 JULY 2004

THERMOPLASTIC ELASTOMER RESIN**TECHNICAL FIELD**

5 The present invention relates to a novel thermoplastic elastomer resin and a process for preparing thereof, which resin is suitable for automobile parts, particularly constant velocity joint boots and bellows, because it has good melt viscosity, melt tension, and thermal resistance. More particularly, the present invention relates to a thermoplastic elastomer resin having good properties and to a process for preparing thereof, which
10 comprises subjecting bisphenol-alt-ethylene glycol oligomer to melt polymerization, and subjecting the polymerized product to reactive extrusion by using hydroxy carboxylic acid compound, diisocyanate, and carbodiimide.

BACKGROUND ART

15

 Polyester-type thermoplastic elastomer (below "TPE") has good oil resistance and chemical resistance as well as excellent low temperature impact property. Thus, it has been widely used in automobile and electric/electronic fields. However, particularly chloroprene rubber (CR), which has been widely used for automobile parts, has poor
20 durability. Thus, recently CR has been replaced with TPE. The use of TPE has been expanded in North America and Europe since it has a good light weight property, resistant-fatigability, chemical resistance, and ozone resistance, compared with CR. Particularly, since TPE for extrusion blowing is produced through blowing procedure in the melting state, resin should have good melt viscosity and melt tension in the melting
25 state, and the thickness distribution of processed product during extrusion blowing should be constant.

 Generally speaking, TPE cannot be subjected to extrusion-blowing due to its low melt viscosity and melt tension in the melting state. The melt viscosity or melt tension of

23 JULY 2004

good melt viscosity, melt tension, and thermal resistance is produced by introducing chain extender and stabilizer for hydrolysis with hydroxy carboxylic acid compound to the polymerized product in order to use it for blowing through increasing the molecular weight, after forming thermoplastic elastomer resin (TPE-A) comprising aromatic dicarboxylic acid, diol having a low molecular weight, polyalkylene oxide, and bisphenol-alt-ethylene glycol oligomer through melt polymerization, in preparing thermoplastic elastomer. The present invention was completed on the basis of the above discovery.

In the present invention, hydroxy carboxylic acid compound that is added at the reactive extrusion maintains the number of hydroxyl group that may react with isocyanate group optimal, thereby to make reactivity of diisocyanate, chain extender, optimal. Also, because carbodiimide is used in order to increase hydrolytic resistance, the chain extender and stabilizer for hydrolysis may fully react with elastomers in the twin screw extruder to produce thermoplastic elastomer having good thermal resistance and no variation in physical property of the product. Also, hardness may be easily and freely controlled by introducing hydroxy carboxylic acid compound at the time of preparing thermoplastic elastomer resin (TPE-B). The hardness of thermoplastic elastomer resin (TPE-B) may be controlled by the content of polyalkyleneoxide that is introduced at the time of preparing thermoplastic elastomer resin (TPE-A). Thus, to produce elastomers with different levels of hardness depending on use, previously polymerization reaction had been carried out by adjusting the content of polyalkyleneoxide. However, the present invention has an advantage that hardness may be controlled through a reaction for a short period of time, instead of controlling the content of polyalkyleneoxide, by using hydroxy carboxylic acid compound at the reactive extrusion.

Therefore, one object of the present invention is to provide thermoplastic elastomer resin (TPE-A) characterized in comprising aromatic dicarboxylic acid, diol having a low molecular weight, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer with polyalkyleneoxide.

23 JULY 2004

It is another object of the present invention to provide thermoplastic elastomer resin (TPE-B) suitable for automobile parts, particularly constant velocity joint boots and bellows since it has good melt viscosity, melt tension and thermal resistance characterized in that it comprises hydroxy carboxylic acid compound, diisocyanate and carbodiimide with the above TPE-A.

It is still another object of the present invention to provide a process for preparing the above thermoplastic elastomer resin (TPE-B).

BEST MODE FOR CARRYING OUT THE INVENTION

Thermoplastic elastomer resin (TPE-A) according to the present invention comprises aromatic dicarboxylic acid, diol having a low molecular weight, polyalkylene oxide, and bisphenol-alt-ethylene glycol oligomer. Thermoplastic elastomer resin (TPE-B) comprises hydroxy carboxylic acid compound, diisocyanate, and carbodiimide, with the above thermoplastic elastomer resin (TPE-A).

Thermoplastic elastomer resin is thermoplastic polymer which hard segment and soft segment is block copolymerized. Thermoplastic elastomer resin (TPE) according to the present invention uses aromatic dicarboxylic acid and diol having a low molecular weight as a hard segment component, and polyalkylene oxide as a soft segment component.

The aromatic dicarboxylic acid may include terephthalic acid (TPA), isophthalic acid (IPA), 1,5-dinaphthalenedicarboxylic acid (1,5-NDCA), 2,6-naphthalenedicarboxylic acid (2,6-NDCA), and dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI), in which diacid is replaced with dimethyl group, and mixture thereof, but DMT is preferable. In preparing thermoplastic elastomer resin (TPE-A) according to the present invention, aromatic dicarboxylic acid is used in the amount of 30 ~ 45 weight%, preferably 33 ~ 40 weight%. If the aromatic dicarboxylic acid is used in the amount less than 30 weight% or

23 JULY 2004

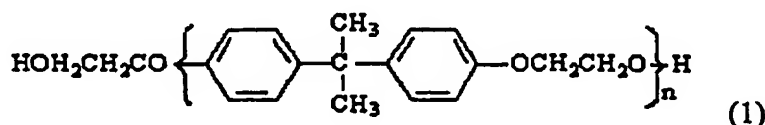
over 45 weight%, the reaction balance is lost to disturb the reaction.

Diol having a low molecular weight according to the present invention includes ethyleneglycol, propyleneglycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, and 1,4-cyclohexanedimethanol, but 1,4-butane diol is preferable. Diol having a low molecular weight is used in the amount of 15 ~ 30 weight%, preferably 20 ~ 25 weight%. If diol having a low molecular weight less than 15 weight% or over 30 weight% is used, the reaction balance is lost to disturb the reaction, as in aromatic dicarboxylic acid.

As polyalkylene oxide may be used polyoxyethylene glycol, polyoxypropylene glycol, polyoxytetramethylene glycol (PTMEG), etc. PTMEG is preferably used among those. Particularly, it is preferable for PTMEG to have a number average molecular weight of 1,000~3,000, and more preferable of 2,000. Generally speaking, the hardness of polyester-type elastomer is expressed by Shore hardness-D (Shore-D), which is determined by the content of polyalkylene oxide. That is, the more the content of polyalkylene oxide is, the lower the hardness (Shore hardness-D) is.

In preparing thermoplastic elastomer resin (TPE-A) according to the present invention, 20 ~ 50 weight%, preferably 30 ~ 45 weight%, of polyalkylene oxide is used. If polyalkylene oxide is present in the amount less than 20 weight%, the hardness of TPE is high, and thus the resistance against wear due to friction in the product after polymer processing gets high. If over 50 weight%, it could be a problem that the thermal resistance of TPE itself is low.

Bisphenol-alt-ethylene glycol oligomer can be represented by the following formula (1):



wherein, n denotes a positive integer of 1 to 5, preferably 1 to 3.

In preparing TPE-A according to the present invention, bisphenol-alt-ethylene glycol oligomer of the above formula (1) reacts with aromatic dicarboxylic acid. A part
5 of aromatic dicarboxylic acid and of hard segment of diol having a low molecular weight is substituted by bisphenol-alt-ethylene glycol oligomer, which makes thermal-resistance good.

When preparing TPE-A according to the present invention, the
10 bisphenol-alt-ethylene glycol oligomer is used in the amount of 0.3 ~ 9.0 weight%, preferably 0.5 ~ 5.0 weight%, more preferably 1.5 ~ 4.0 weight%. In case that bisphenol-alt-ethylene glycol oligomer is less than 0.3 weight%, the improvement of elastic recovery rate and processability is insignificant. In case that over 9.0 weight%, it is difficult to control the hardness of TPE.

15 For the thermoplastic elastomer resin (TPE-A) according to the present invention, additives such as branching agent may also be used. Branching agent may increase the melt viscosity and melt tension of elastomer. As branching agent, glycerol, pentaerythritol, neopentylglycol, etc., preferably glycerol, may be used in the amount of
20 0.05 ~ 0.10 weight%. If the branching agent is less than 0.05 weight%, it is hard to expect the increase of melt viscosity. If over 0.10 weight%, the melt viscosity of TPE-A is so overly raised that it is difficult to control the inherent viscosity at melting polymerization.

25 The preparation process of thermoplastic elastomer resin (TPE-A) according to the present invention consists of two steps, oligomerization and polycondensation. Oligomerization is carried out at 140 ~ 215 °C for 3~4 hours by using 0.025 ~ 0.03 weight% of titanium butoxide (TBT) as catalyst. Polycondensation is processed by reducing the pressure stepwise from 760 torr to 0.3 torr.

30 In the above polycondensation, tetrahydroxyfuran (THF), which is highly volatile

23 JULY 2004

and may cause appearance defect of the processed product due to generation of smell and gas at polymer processing, may be generated by the decomposition of PTMEG. Thus, the present invention uses such a polycondensation process that in order to suppress the generation of THF up to the maximum, the pressure is reduced from 760 torr to 0.3 torr for 1 hour, the vacuum condition of 0.3 torr or less is applied for additional 3 ~ 4 hours, the temperature of reactor is raised from 210 °C to 250 °C for 2 hours, and the final temperature of 250 °C is maintained for the remaining 2 ~ 3 hours.

Branched polyester-type elastomer (TPE-A) is prepared according to the above melt polymerization, with containing 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer, represented by the formula (1). TPE-A is obtained by predicting its molecular weight on the basis of Torque applied to the stirrer of polycondensation reactor. The molecular weight of obtained thermoplastic elastomer resin (TPE-A) is expressed by its inherent viscosity (I.V). Its inherent viscosity has a value of 1.6 ~ 1.8 dl/g when measured in the solvent of 50/50 of phenol/tetrachloroethane (TCE).

TPE-A according to the present invention has a good elastic recovery rate and processability, compared with TPE without bisphenol-alt-ethylene glycol oligomer. That is, TPE-A can be processed at a low temperature since the melting temperature of resin is lowered by 10 ~ 20 °C compared with TPE without bisphenol-alt-ethylene glycol oligomer. It is desirable that the Melt Index (MI) of TPE-A has a range of 13 ~ 17g/10min under 230 °C and 2.16 kg, preferably 14 ~ 16g/10min.

Furthermore, because bisphenol-alt-ethylene glycol oligomer lowers the melting temperature of TPE-A, TPE-A has good processability since its processing temperature at polymer processing after extrusion is low compared with TPE polymerized by only aromatic dicarboxylic acid, diol having a low molecular weight, and polyalkylene oxide. However, TPE-A itself has still such low melt viscosity or melt tension that it does not have optimal physical property

in the range of 35 ~ 70 mN, preferably 40 ~ 60 mN. The Melt Extension less than 35mN results in the decrease of thickness distribution and shape stability at the time of extrusion blowing, and more than 70mN results in the decrease of productability.

5 5. Melt Viscosity

Melt Viscosity is measured at the respective temperature of 230 °C, 240 °C and 250 °C within the range of extrusion shear rate by using RDS (Rheometric Dynamic Spectrometer).

10 6. Heat Distortion Temperature (HDT)

HDT of 1/4"specimen is determined under 4.16 kgf/cm² according to ASTM D 648.

7. Elastic Recovery Rate

15 A machine specimen injected by ASTM D 638 is installed to the jig by temperature, and the Elastic Recovery Rate of the specimen is measured after thermal treating for a desired time. Elastic Recovery Rate is determined as a ratio of the angle of specimen after annealing to the angle of specimen before annealing.

20 8. Impact Strength

Impact Strength is measured according to ASTM D 256 at both room temperature (23 °C) and low temperature (-40 °C).

9. Mechanical Physical Property

25 Tensile property and flexion property are determined according to ASTM D 638,790.

Example 1

30 34.6 weight% of DMT, 21.2 weight% of 1,4-butane diol, 40.2 weight% of PTMEG having the molecular weight of 2,000, 3.8 weight% of bisphenol-alt-ethylene glycol oligomer (n=1, HanNong

23 JULY 2004

The composition and physical properties of the obtained TPE-B are listed at Tables 1 and 2 below.

Example 3

5 TPE-A is prepared according to the same procedure as Example 1 except that in the oligomerization, 36.3 weight% of DMT, 23.4 weight% of 1,4-butane diol, 39.7 weight% of PTMEG having the molecular weight of 2,000, 0.4 weight% of bisphenol-alt-ethylene glycol oligomer (n=1, HanNong WhaSung Koremul-BSA-20), and 0.065 weight% of glycerol are added to the oligomerization reactor, and 0.025 weight% of
10 TBT, a catalyst, is further added. Thereafter, in the polycondensation, 0.04 weight% of TBT, a catalyst, and 0.07 weight% of Irganox 1010, thermal stabilizer, are introduced to carry out the polycondensation. By using TPE-A thus obtained, TPE-B is prepared as the same composition as Example 1. The composition and physical properties of TPE-B thus obtained are listed in Tables 1 and 2 below.

Example 4

15 TPE-A is prepared according to the same procedure as Example 1 except that in the oligomerization, 33.1 weight% of DMT, 19.3 weight% of 1,4-butane diol, 40.6 weight% of PTMEG having the molecular weight of 2,000, 6.8 weight% of
20 bisphenol-alt-ethylene glycol oligomer (n=1, HanNong WhaSung Koremul-BSA-20) and 0.059 weight% of glycerol are introduced to the oligomerization reactor, and 0.028 weight% of TBT, a catalyst, is further added. Thereafter, in the polycondensation, 0.043 weight% of TBT, a catalyst, and 0.07 weight% of Irganox 1010, thermal stabilizer, are added to carry out the polycondensation. By using TPE-A thus obtained, TPE-B is
25 prepared as the same composition as Example 1. The composition and physical properties of thus obtained TPE-B are listed in Tables 1 and 2 below.

Comparative Example 1

The same procedure as Example 1 is applied except that 96 weight% of TPE-A
30 prepared according to the same procedure as Example 1 is used and PBT is not used. The

23 JULY 2004

obtained without bisphenol-alt-ethylene glycol oligomer is used and PBT is not used.
The composition and physical properties of thus obtained TPE-B are listed in Tables 1 and 2 below.

5 Table 1

	TPE-B						
	TPE-A	TPE*	PBT	diisocyanate	carbodiimide	additional additive**	retention time
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(sec.)
Ex. 1	93		3	1.0	0.2	2.8	50~60
Ex. 2	76		20	1.0	0.2	2.8	50~60
Ex. 3	93		3	1.0	0.2	2.8	50~60
Ex. 4	93		3	1.0	0.2	2.8	50~60
Comp. Ex. 1	96		0	1.0	0.2	2.8	50~60
Comp. Ex. 2	66		30	1.0	0.2	2.8	50~60
Comp. Ex. 3	93		3	0	0	4.0	50~60
Comp. Ex. 4	93		3	0	0.2	3.8	50~60
Comp. Ex. 5	93		3	1.0	0.2	2.8	40
Comp. Ex. 6		96	0	1.0	0.2	2.8	50~60

* TPE: TPE polymerized without bisphenol-alt-ethylene glycol oligomer

** Additional additives: thermal stabilizer, antioxidant, lubricant, silicone-type master batch, and carbon black master batch

10 PBT: n=80~90, TRIBIT 1500 manufactured by Sam Yang Corp.

Diisocyanate: Lupranate MM103C manufactured by BASF

Carbodiimide: Stabaxol 1 manufactured by Bayer

Thermal stabilizer: 412S manufactured by SHIPRO Kasei Corp.

Antioxidant: Songnox 1076 manufactured by SongWon Industrial Corp.

15 Lubricant: EP861 manufactured by HENKEL Corp.

Silicone-type master batch: MB-50-010 manufactured by DOW CORNING Corp.

Carbon black master batch: BKA2 manufactured by Hyun Jin Chemical Co.

Table 2

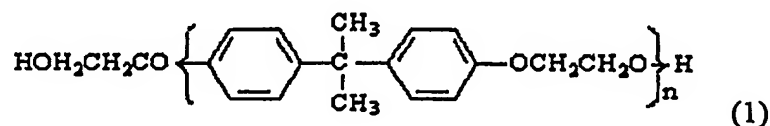
23 JULY 2004

INDUSTRIAL AVAILABILITY

The polyester-type thermoplastic elastomer resin prepared by reactive extrusion by using hydroxyl carboxylic acid compound, diisocyanate, carbodiimide, and additional
5 additives, after melt polymerization using bisphenol-alt-ethylene glycol oligomer according to the present invention, shows improved melt viscosity and melt index that results in good extrusion property, thermal resistance, chemical resistance, and durability, suitable for various automobile parts, particularly constant velocity joint boots and various bellows.

CLAIMS

1. Thermoplastic elastomer resin (TPE-A) which comprises 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer, represented by the following formula (1):



wherein n denotes a positive integer of 1 to 5.

2. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the inherent viscosity(I.V.) of TPE-A is 1.6 ~ 1.8 dl/g.
3. The thermoplastic elastomer resin (TPE-A) of claim 1, further comprising 0.05 ~ 10 weight% of glycerol.
4. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the aromatic dicarboxylic acid is selected from a group consisting of terephthalic acid, isophthalic acid, 1,5-dinaphthalenedicarboxylic acid, 2,6-dinaphthalenedicarboxylic acid, dimethyl terephthalate, dimethyl isophthalate, and mixtures thereof.
5. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the diol having a low molecular weight is selected from a group consisting of ethylene glycol, propylene glycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,4-cyclohexane dimethanol, and mixtures thereof.
6. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the polyalkylene oxide is selected from a group consisting of polyoxyethylene glycol,

23 JULY 2004

11. The thermoplastic elastomer resin (TPE-B) wherein the melt index ratio (MIR) is 1.0 ~ 1.5.

5

12. The thermoplastic elastomer resin (TPE-B) wherein the inherent viscosity of PBT is 0.7 ~ 1.3 dl/g.

10

13. A process for preparing thermoplastic elastomer resin (TPE-B) which comprises:
(a) melt polymerization of 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer defined in claim 1, and 0.05 ~ 0.10 weight% of glycerol, to prepare TPE-A; and
(b) reactive extrusion of 66 ~ 96.85 weight% of TPE-A prepared in the above (a), 0.1 ~ 5.0 weight% of diisocyanate, and 0.05 ~ 1.0 weight% of carbodiimide, to prepare TPE-B.

15

14. The process of claim 13 wherein the diisocyanate is the modified product of 4,4-diphenylmethane diisocyanate defined in claim 10.

20

15. The process of claim 13 wherein the retention time in extruder in step (b) is between 50 and 80 seconds.